Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

A passive dosing method to determine fugacity capacities and partitioning properties of leaves

Supplementary Information

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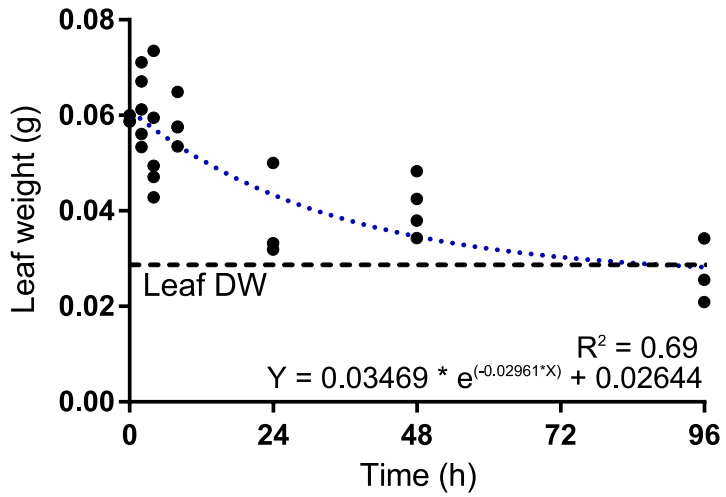

Figure s1: Loss of water from the leaves over time during the exposure to the PDMS donor disks. The leaf dry weight (DW) is indicated by the broken horizontal black line and the dotted blue curve shows a one-phase decay curve that was fitted to the measured data.

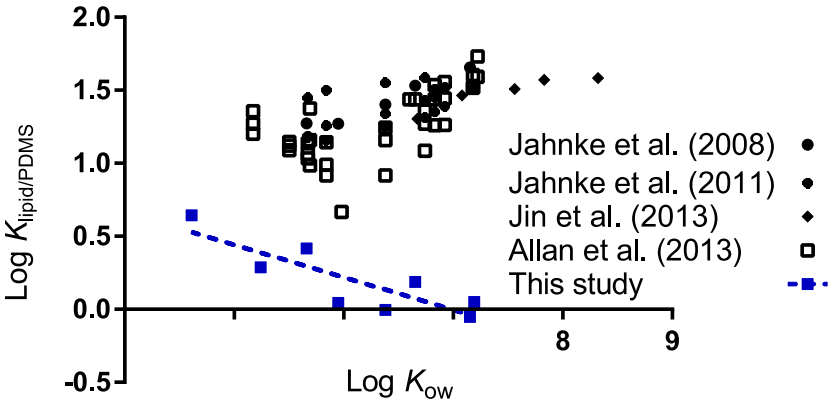

Figure s2: Lipid/PDMS partition ratios (log $K_{lipid/PDMS}$) plotted vs. the chemicals' log K_{OW}. Comparison between our data normalized to the extractable organic matter fraction of rhododendron leaves and literature data for $K_{lipid/PDMS}$. Data from Jahnke et al. (2008) are the average $K_{lipid/PDMS}$ measured for Tobis fish oil, seal oil and olive oil.[1], data from Jahnke et al. (2011) were derived from equilibrium concentrations measured for Norwegian Atlantic salmon and Baltic Sea eel.[2] Data from Jin et al. (2013) are $K_{lipid/PDMS}$ for dugong blubber[3] and data from Allan et al. (2013) were measured for brown trout.[4]

Tables

Table s1: Details of the solvents used in this study.

Type	Purity	Vendor
Acetone	Suprasolve	Merck, Darmstadt, Germany
Isooctane	Suprasolve	Merck, Darmstadt, Germany
Acetonitrile	Chromasolve	Sigma-Aldrich, Missouri, U.S.

Table s2: *m/z* used for quantification and retention time of the analytes and internal standards (see also *Text s2* for more information on the analysis).

Analyte	Ions monitored (*m/z*)	Retention time (min)
PCB 3	188, 190	7.21
PCB 4	222, 224	7.56
PCB 28	256, 258	10.42
PCB 28 C13	268, 270	10.42
PCB 53	290, 292	10.57
PCB 52	290, 292	11.17
PCB 101	326, 328	13.13
PCB 101 C13	338, 340	13.13
PCB 118	326, 328	14.56
PCB 138	360, 362	15.64
PCB 138 C13	372, 374	15.64
PCB 180	394, 396	17.13
PCB 180 C13	406, 408	17.13

Table s3: MQLs for both matrices and the fraction of blanks in which the compounds were detected.

Compound	Leaves (ng/g dry leaf)		PDMS (ng/g PDMS)	
	MQL	Presence in blanks	MQL	Presence in blanks
PCB 3	112	9/13	10.6	0/8
PCB 4	169	0/13	886	5/8
PCB 28	80.6	8/8	509	8/8
PCB 52	152	13/13	450	7/8
PCB 101	96.6	0/13	440	7/8
PCB 118	197	1/13	716	1/8
PCB 138	27.8	2/13	520	8/8
PCB 180	300	1/13	427	8/8

Table s4: Recoveries of the labeled internal standards.

		Recoveries (%)			
		PCB 28	PCB 101	PCB 138	PCB 180
Leaves	All	80.5	69.3	75.5	70.9
PDMS	Blanks	105	119	116	109
	Samples	137	145	155	149
	All	128	133	138	138

Table s5: Estimated fraction of the PCBs in the PDMS/leaf sandwich present in the leaves at equilibrium.

Compound	% of total PCB mass present in leaf at equilibrium
PCB 3	6.4
PCB 4	3.0
PCB 28	3.9
PCB 52	1.7
PCB 101	1.8
PCB 118	2.7
PCB 138	1.8
PCB 180	1.6

Additional text

Text s1. Extraction procedure using QuEChERS

The dispersive SPE (dSPE) procedure with QuEChERS was as follows: The leaf homogenate in 1 mL of acetonitrile and the stainless steel ball were transferred to a new vial and the original vial used for homogenization was washed 3 times with acetonitrile to increase the recovery of the analytes. The vial containing the homogenate was then transferred to an ice bath and 10 mL of MilliQ water and 9 mL of acetonitrile were added to the sample. This was followed by the addition of the non-buffered method extraction kit, containing 4 g of magnesium sulfate ($MgSO_4$) and 1 g of sodium chloride (NaCl), and the mixture was vortexed for 30 seconds. The vortexed sample was then centrifuged for 5 minutes at 4000 RPM and the supernatant was transferred to a new vial. To the original sample, a 10 mL aliquot of acetonitrile was added, the vial was vortexed, centrifuged and the supernatant added to that from the previous step. The combined supernatants were then reduced to a final volume of 1 mL using a gentle stream of nitrogen. This extract was transferred to a 2 mL dSPE tube containing 150 mg $MgSO_4$, 50 mg PSA (primary-secondary amine) and 50 mg GCB (graphitized carbon black), vortexed for 30 seconds and centrifuged for 5 minutes at 4000 RPM. The supernatant was then transferred to a GC vial and the process was repeated by adding a small amount of acetonitrile to the original dSPE tubes and combining the supernatants after centrifugation. 50 ng of PCB 53 was added and the samples were analyzed using GC/MS.

Text s2. GC/MS analysis

The sample analysis was performed using a 30 m TG-5SILMS column with an inner diameter of 0.25 mm and a film thickness of 0.25 µm coupled to a Trace 1310 GC and ISQ LT MS (Thermo Scientific, U.S.). The oven program was set to start at 70 °C, hold for 1 minute, ramp to 160 °C at 40 °C/minute, hold again for 1 minute, ramp to 266 °C at 8 °C/minute and finally ramp to 320 °C at 50 °C / minute with a hold time of 5 min. 1 µL of the samples was injected in a Programmable Temperature Vaporization (PTV) injector set at 250 °C and run in splitless mode with a constant carrier gas flow rate of 1 mL/min. The MS was set to work in electron impact (EI) mode with selective ion monitoring (SIM). The temperature of the ion source was set at 250 °C and the transfer line was kept at 300 °C. The analytes and ions used for the quantification process are given in *Table s2*. The areas of two *m/*z were summed up for the quantification of each compound to achieve higher intensities and lower levels of noise on the MS. The ratio of both ions was compared regularly to that in the standards to ensure proper identification.

Text s3. Propagation of uncertainty for the data presented in Table 1

The quantifiable uncertainties were dominated by our measurements of $K_{leaf/PDMS}$ and those of log K_{aw}[5]. The literature cited in this study[6] reports limited variability in the measurements of PDMS/water partition ratios; hence we assumed that those are negligible.

To propagate the uncertainty in our measurements we first calculated the relative standard deviation for K_{aw} from the recommended confidence factors given by MacLeod et al. for the vapor pressure and water solubility[5] using *equation s1*:[7]

Eq. s1 $$Rel.Stdev. = \sqrt{e^{\left(\frac{\ln(2)Cf}{1.96^2}\right)} - 1}.$$

We then propagated this uncertainty into our measurements of Z_{leaf} by using *Equation s2*:

Eq. s2 $$Rel.Stdev.Z_{leaf} = \sqrt{(Rel.Stdev.\ K_{aw})^2 (Rel.Stdev.\ K_{leaf/PDMS})^2}.$$

As the uncertainty for $K_{PDMS/water}$ and $K_{PDMS/air}$ was assumed to be negligible, the relative standard deviation of Z_{leaf} was also used to estimate the uncertainty for $K_{leaf/water}$ and $K_{leaf/air}$.

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